CRANBERRY INSTITUTE GRANT FINAL REPORT
Phase 1 Laboratory Studies

Use of Lignocellulosic Materials as Sorbents for Pesticide and Phosphate Residues

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ABSTRACT

The ability of lignocellulosic materials to remove pesticides (dichlobenil, chlorothalonil, chlorpyrifos) or phosphate anions from water was evaluated under dynamic conditions by percolating water solutions of pesticides through glass columns packed with the lignocellulosic materials or under static conditions, by equilibrating the lignocellulosic materials, in batch experiments, with water solutions of potassium dihydrogenphosphate in glass beakers. The percent removal of the pesticides varied from 12% to 96%. The percent removal of phosphate anions varied from less than 10% to 88%. The ability of lignocellulosic materials to remove pesticides or phosphate anions from water compares favorably with that of granular activated carbon.

1. INTRODUCTION

Cranberry growers are concerned about the environmental impact of residual pesticide and phosphate fertilizer runoff on surface waters. Some growers have placed activated carbon filters in flumes and ditches to remove any pesticide residues that may be present. Since activated carbon is prohibitively expensive, alternate low-cost sorbents are required to prevent pesticide and phosphate runoff from discharging into surface waters.

The long-term goal of this project is to develop low-cost filtration sorbents from modified lignocellulosic materials. Such filtration systems can be used by the cranberry industry to remove residual pesticides and phosphate from irrigation water before discharge into surface waters.

The ultimate benefit that the public will derive from this project is the protection of water resources from accumulating pesticides and excessive nutrients, both of which may be detrimental to aquatic vitality. The use of low cost sorbents derived from renewable resources will hopefully reduce the cost of maintaining acceptable water quality standards.

This project is a significant contribution to the efforts of the cranberry industry to develop economical and ecologically sound production practices.

2. EXPERIMENTAL

a. Materials and Methods

The sorbent materials were prepared from waste bark or wood from southern yellow pine, eastern hemlock, poplar, beech or red maple; waste alfalfa fiber; waste cranberry pulp mixed with rice hulls; granular activated carbon (4 – 14 mesh); clays and metal oxides.
The bark or wood-based sorbent materials were used in the form of 60/80 mesh particles. The waste alfalfa fiber, cranberry pulp mixed with rice hulls, clays and metal oxides were used without further fractionation. All of the sorbent materials were washed exhaustively with water before use.
The surface chemistry of the bark particles was modified by extraction with an aqueous solution of N-methyl pyrrolidone followed by treatment with one of the following reagents:
- Methanolic potassium hydroxide

- Stearic acid
- Aqueous poly (allylamine hydrochloride) and epichlorohydrin

The surface chemistry of the wood particles was modified by extraction with toluene/ethanol (2/1 v/v) followed by ethanol, boiling water, and tetrahydrofurfuryl alcohol. The waste alfalfa fiber was recovered from cow manure by exhaustive washing with water. The surface chemistry of the waste cranberry pulp mixed with rice hulls was modified by exhaustive washing with water, followed by treatment with (3-chloro-2-hydroxypropyl) trimethylammonium chloride.

Pesticide sorption experiments:

A 2-gram sample of the sorbent material, weighed accurately to two decimal places, was placed in a 10.5 X 300 mm glass column and allowed to equilibrate overnight under water. The sorbent bed in the column was rinsed with five column volumes of water before 500 ml of water, containing 100 ppb each of dichlobenil, chlorothalonil and chlorpyrifos, was percolated through it under gravity flow.

Pesticide analysis in column effluent:

The column effluent was concentrated by solid phase extraction on a C-18 cartridge. The concentration of the pesticides in the extract was determined by gas chromatography with mass selective detection (GC-MSD), using a 30-meter DB5-MS capillary column equipped with a 5-meter megabore capillary guard column.

Phosphate sorption experiments:

A 0.5 or 1-gram sample of the sorbent material was placed in 50 mL of a water solution containing 0.5-500 mg/L of potassium dihydrogenphosphate in a beaker equipped with a lid. The mixture was shaken at 150 rpm on an oscillating shaker for 48 hours at room temperature.

Phosphate analysis in filtrate:

The supernatant solution of potassium dihydrogenphosphate that had been equilibrated with the sorbent material was passed through a 0.45 μm nylon syringe filter. The phosphate concentration in the filtrate was measured by the standard colorimetric Ascorbic Acid Method.

b. Results and Discussion

Pesticide removal:

The efficiency of pesticide removal from water by some of the sorbents is summarized in Table 1. The removal efficiency is calculated as the percent pesticide removed from the water solution by the following equation:

$$\text{Removal Efficiency} = 100(C_{in} - C_{out})/C_{in} \qquad (1)$$

where C_{in} and C_{out} are the column influent and effluent concentrations of the pesticide.

Table 1. Pesticide Removal Efficiency from Water by Various Lignocellulosic Sorbents

Sample[1] No.	Sorbent ID	% Removal Dichlobenil	% Removal Chlorothalonil	% Removal Chlorpyrifos	% Removal Phosphate
1	B4-58-130	90	88	92	nd[2]
2	MBR79-31	70	91	96	nd
3	B94-116	41	90	95	nd
4	BSC6-23	39	84	88	nd
5	BST103-155R	95	91	92	nd
6	BFS106-164	59	88	95	nd
7	BFC97-124	12	14	38	nd
8	BHG138-78	82	92	96	57-88
9	THFASYP-397	37	82	93	nd
10	HMDSOSYP3497	56	83	96	nd
11	BUT04-97	29	81	89	nd
12	BEE4-21-97	49	70	77	nd
13	Eastern hemlock	nd	nd	nd	< 10
14	Poplar	nd	nd	nd	< 10
15	Beech	nd	nd	nd	< 10
16	Red Maple	nd	nd	nd	< 10
17	GAC	51	72	85	18-40
18	WCM18-45	54	88	51	nd
19	RHC130-65	23	53	60	nd
20	SSFA8-27	31	86	86	nd
21	KBC/ZnO	18	-15	15	60-80

Notes: [1]Samples 1-8 are modified bark particles from southern yellow pine; samples 9-12 are modified wood particles from southern yellow pine; sample 13 is a softwood; samples 14-16 are particles from hardwood species; sample 17 is granular activated carbon; sample 18 is fiber recovered from cow manure; sample 19 is modified waste cranberry pulp mixed with rice hulls; sample 20 is enzyme modified alfalfa fiber; sample 21 is a clay-based sorbent.
[2]nd = not determined.

Among the sorbents derived from bark, sample 5, showed the highest removal efficiency for all three pesticides. In general, the sorbents derived from bark showed better pesticide removal efficiency compared to the sorbents derived from wood (samples 9 to 16). In addition, the sorbents derived from bark showed better pesticide removal efficiency compared to the sample of granular activated carbon. However, in contrast to the other lignocellulosic sorbents, granular activated carbon also showed comparatively higher removal efficiency for phosphate.

Phosphorus removal:

The efficiency of phosphorus removal from water by some of the sorbents is shown in Table 1 and Figure 1. The removal efficiency is calculated as the percent dissolved phosphorus removed from the water solution by the following equation:

$$\text{Removal Efficiency} = 100(C_0 - C_e)/C_0 \qquad (2)$$

where C_0 and C_e are the initial and final concentrations of dissolved phosphorus in the supernatant liquid equilibrated with the sorbent material.

The phosphate removal efficiency was determined for a bark-based hydrogel (Sample 8 in Table 1); for unmodified wood particles (Samples 13 – 16 in Table 1); and for granulated activated carbon (Sample 17 in Table 1). The bark-based hydrogel showed a phosphorus removal efficiency of 57 – 88% in the concentration range, 0.5 to 100 mg/L. The granular activated carbon showed a phosphorus removal efficiency of 18 – 40%. The unmodified wood particles showed a phosphorus removal efficiency of less than 10%. Since such low phosphorus removal efficiencies are inadequate, other sorbent materials were also evaluated. These included ash obtained from aspen, metal oxides or clays. The phosphorus removal efficiencies of these sorbents are compared in Figure 1. Aspen ash showed the highest removal efficiency, for the three phosphorus concentrations, 10, 50 and 500 mg/L. The next highest was zinc oxide (ZnO), followed by Kentucky Ball Clay (KBC).
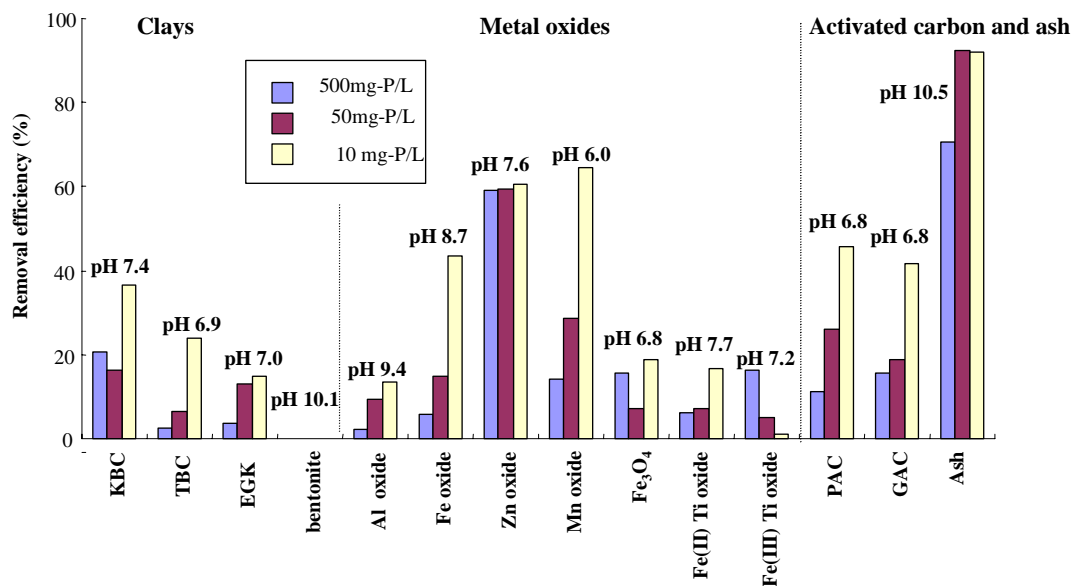
Figure 1. Phosphate removal efficiency of clays, metal oxides, activated carbon and ash.

Notes: KBC = Kentucky Ball Clay; TBC = Tennessee Ball Clay; EGK = English Kaolin; PAC = Powder Activated Carbon; GAC = Granular Activated Carbon.

A composite sorbent formulated from KBC and ZnO was also evaluated. The rationale for evaluating composite materials was to take advantage of the synergistic effect of using high cost metal oxides with high phosphate affinity in combination with low cost clays with moderate phosphate affinity. The KBC/ZnO composite was used in the form of a pellet. The KBC/ZnO pellets showed phosphate removal efficiency of approximately 60 - 80%. Additional studies are required to design a suitable procedure for pelletizing KBC/ZnO composites in larger scale.

3. Conclusions

In the current phase of this project we have demonstrated that it is possible to use lignocellulosic sorbents for removing pesticides from water solutions of pesticides prepared in the laboratory. The next step is to demonstrate the feasibility of this technology on field water samples. For that purpose it is necessary to develop pilot scale methods for modifying selected lignocellulosic materials in larger batches. It is envisaged that larger batches will allow the design of filtration systems that could be used in limited field trials.

We have also demonstrated that lignocellulosic sorbents have comparatively low removal efficiencies for phosphorus. Hence we have evaluated other sorbents based on clay and metal oxides. Although KBC/ZnO composite is a promising sorbent for phosphate anions, further studies are required to develop suitable methods for making it into pellets. In addition, the use of ZnO may be undesirable because of the possibility of zinc leaching into the environment. Thus other additive metal oxides such as aluminum oxide (Al_2O_3) need to be evaluated.

Knowledge of the mechanism of pesticide or phosphorus sorption by lignocellulosic materials is still incomplete. Further studies are required to determine the sorption kinetics, breakthrough points of the solutes, and the effect of natural organic material and other variables such as pH on the sorption capacity of these materials.

Completion of this project will likely lead to the development of cost-effective technologies for producing low cost sorbent materials for removing runoff pesticides or excessive nutrients from water discharged from cranberry bogs. This in turn will benefit the growers by keeping the cost per barrel of producing cranberries at reasonable levels while protecting the quality of surface waters.